

Photon Energy Dependence of the High Resolution C 1s Photoelectron Spectrum of CO in the Threshold Region

K. J. Randall,* A. L. D. Kilcoyne, H. M. Köppe, J. Feldhaus, and A. M. Bradshaw
Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin (Dahlem), Federal Republic of Germany

J.-E. Rubensson and W. Eberhardt
Institut für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, 52425 Jülich, Federal Republic of Germany

Z. Xu and P. D. Johnson
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

Y. Ma
Pacific Northwest Laboratory, Richland, Washington 99352
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The C 1s photoelectron spectrum of CO has been measured with high resolution in the threshold region. The data exhibit hitherto unresolved vibrational structure on the C 1s main photoelectron line as well as new features in the satellite region. The vibrational energy of the CO⁺ ion is 301 ± 3 meV. The vibrational structure changes dramatically with photon energy due to the influence of the σ^* shape resonance. The new satellite lines which are not present at high photon energies are attributed to conjugate shakeup processes.

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Molecular core level photoionization is generally accompanied by vibrational excitations because the creation of the core hole leads to a strong rearrangement of the electron density distribution within the molecule and hence to changes in the molecular potential [1]. This so-called relaxation is also responsible for additional electronic excitations in the valence electron shell, known as shakeup transitions, which manifest themselves as satellite peaks in the photoelectron spectrum [2]. One of the most interesting aspects of these phenomena is the dependence on photon energy in the near threshold region where strong resonances often dominate the photoionization cross sections. Particularly shape resonances, which are caused by temporary trapping of the photoelectron in the effective molecular potential, are known to be very sensitive to bond length and details of the potential [3-5]. Photon energy dependent measurements of the vibrational structure in the near threshold region are therefore important for obtaining a deeper understanding of shape resonance behavior. Such experiments have recently been performed in the valence ionization region [6-8], but the lack of suitable high-flux, high-resolution monochromators at synchrotron radiation sources has prevented similar studies in the core level region. This is unfortunate because core level shape resonances are particularly useful in the characterization of adsorbed molecules. Similarly, attempts to understand the near threshold behavior of shakeup satellites have been thwarted by insufficient sensitivity, poor resolution, and high background. The few experiments that have been reported in the literature clearly show that very different satellite behavior can be found near threshold [9-12], but it is not clear what influence shape resonances have on shakeup satellites and

which role is played by conjugate shakeup processes. In simple terms, the latter can be understood as dipole transitions of a core electron to a bound state accompanied by the excitation of a valence electron into the continuum.

In this Letter we report photoemission data in the region of the σ^* shape resonance above the C 1s threshold of CO. Vibrational structure in the C 1s main photoelectron line is clearly resolved and an accurate value for the vibrational energy is determined. Further, as expected from theoretical work on valence photoionization [4,5], a significant energy shift of the shape resonance is observed for different vibrational states. Finally, the energy dependence of the satellite spectrum demonstrates dramatically the strong influence of conjugate shakeup near threshold, ending a long discussion in the literature [9,10,13].

The measurements were performed on the new spectroscopy beam line X1B on the X1 undulator in Brookhaven [14]. The photoelectrons were analyzed by a commercial PHI-15-255G double-pass cylindrical-mirror analyzer (CMA) oriented perpendicular to the storage ring plane. In this geometry the measured intensity depends on the angular distribution of the photoelectrons: For the same cross section but different angular distributions the measured intensity can be up to 16% larger and 31% smaller than that measured for isotropic emission. We could therefore not determine cross sections directly in the present study, but the effects observed are so large that the essential conclusions are unaffected. The combined monochromator and CMA resolution was typically 150 meV for the C 1s main line spectra and 200 meV for the satellite region.

Figure 1 shows two spectra of the C 1s main photoelectron line of CO at photon energies of 303.7 and 311.9 eV,

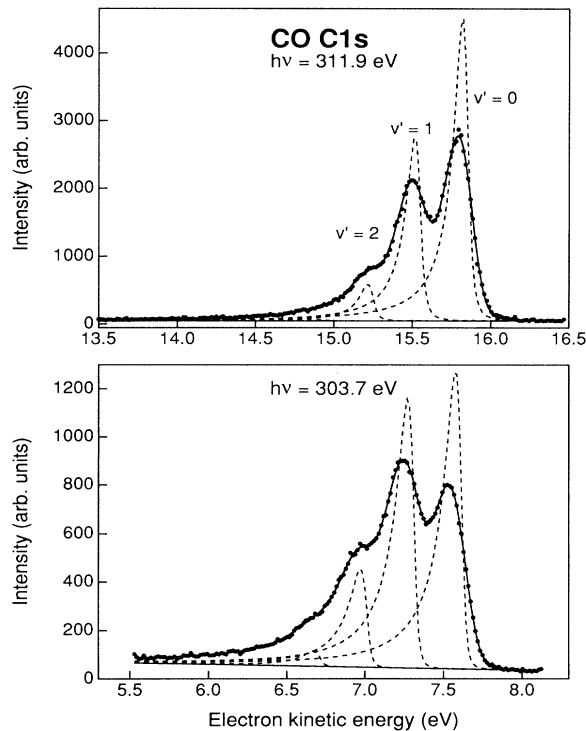


FIG. 1. The C 1s main photoelectron line of CO measured at photon energies of 311.9 eV (top) and 303.7 eV (bottom), showing vibrational fine structure.

i.e., near the shape-resonance maximum and above the shape resonance, respectively. Also shown are the results of a nonlinear least squares fit described in more detail below. Clearly, higher vibrational states are strongly enhanced on the shape resonance. In order to obtain a more complete picture, however, we have measured a series of spectra covering the energy range of the shape resonance from 300 to 320 eV. To determine the influence of monochromator and CMA transmission on the line profile, we have also measured argon 2*p* spectra (for which the natural linewidth is known [15]) in the same range of photoelectron kinetic energies. The analysis of the argon data indicates that the measured line shape is dominated by postcollision interaction (PCI), i.e., the interaction of the photoelectron with the emitted Auger electron. The fast Auger electron can take up some of the kinetic energy of the slow photoelectron, leading to asymmetric, energy shifted line profiles which depend on the electron energies and on the core hole lifetime. The measured argon 2*p* lines are very well described by a convolution of a slightly skewed Gaussian (i.e., a Gaussian with two different half-widths) for the instrument function with the analytical PCI line shape derived by Kuchiev and Sheinerman [16]. All the data were analyzed using a least squares fitting routine. Since the PCI profile changes systematically with photon energy better results were obtained by simultaneously fitting spectra

measured at different photon energies assuming the same vibrational energy spacings and the same core hole lifetime. Even in these coupled fits there still remains a small correlation between the lifetime, the average energy assumed for the Auger electrons, and the width and skewness of the experimental profile. This correlation does not noticeably affect the energy positions and relative intensities but does have a significant influence on the resulting lifetime. We therefore give only a preliminary value for the C 1s core hole lifetime width of $\gamma = 90 \pm 15$ meV. This is larger than the value of 73 meV recently calculated by Coville and Thomas [17]. A more accurate study of lifetimes for a series of different molecules under better defined experimental conditions has recently been performed and will be analyzed shortly. The decomposed and deconvoluted vibrational fine structure shown as dashed lines in Fig. 1 graphically demonstrates the strong asymmetry characteristic of PCI which persists up to several tens of eV above threshold.

The transition energy between the vibrational ground state, $v' = 0$, and the first excited state, $v' = 1$, of C 1s ionized CO is determined to be 301 ± 3 meV. This value is slightly smaller than the one expected from the $Z + 1$ equivalent core model for the ground state of NO^+ (307.5 meV, with a correction for the different reduced masses [13]). This difference could not be discerned in a recent experiment using high resolution zero-kinetic-energy (ZEKE) photoelectron spectroscopy [13] because at threshold PCI leads to a severe distortion of the spectrum. In that study a value of 308.7 ± 17.4 meV was reported. In earlier measurements using monochromatized Al $K\alpha$ radiation the vibrational fine structure could not be resolved [1]. The calculations of Clark and Müller [18] and Correia *et al.* [19] indicated vibrational energies of 330 and 322 meV, respectively, which may be due to the fact that the complicated relaxation effects were not fully accounted for.

The intensities of the individual vibrational components of the CO C 1s photoelectron line in the region of the σ^* shape resonance are presented in Fig. 2. Note that these intensities are normalized such that the sum of the vibrational components for each photon energy gives the cross section obtained for the unresolved C 1s photoelectron line [20]. In the region of a shape resonance relative variations of the angular distribution for different vibrational states are expected theoretically [4,5] and have been observed experimentally in valence photoelectron spectra [6-8]. Since these variations are normally not very large, the influence on the measured intensities is probably small (even though we do not measure at the "magic angle") and thus the intensities of Fig. 2 should be close to the partial cross sections. Clearly the strong relative enhancement of the $v' = 2$ line cannot be explained by a change in the angular distribution. These results therefore indicate that the σ^* shape resonance of CO is shifted to lower energies for higher vibrational states. It is this resonant intensity enhancement at dif-

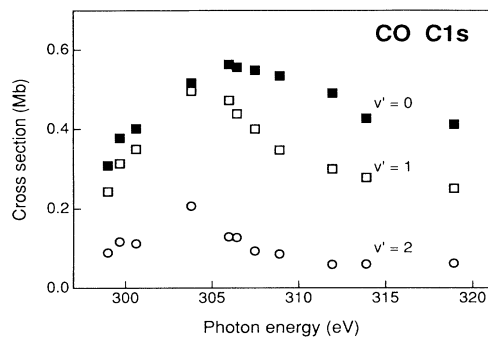


FIG. 2. Intensity of the three lowest vibrational bands, normalized to the partial cross section of the unresolved C 1s main line of Ref. [20] (see text).

ferent energies for different v' that leads to a strong perturbation of the Franck-Condon (FC) vibrational intensity distribution in this energy region. Consequently, we cannot use our present data for a simple FC analysis to determine a precise value for the internuclear distance R_e of C 1s ionized CO⁺; measurements at still higher photon energies are necessary. However, we can assume that the ion is considerably contracted because the vibrational energy of 301 meV is much higher than that of the neutral ground state (268.82 meV [21]). A shorter R_e for the ion is also consistent with the observation that the shape resonance shifts to lower energies for increasing v' : The average internuclear distance is larger for molecules excited to higher vibrational states v' , consequently, the shape resonance occurs at lower energies [4,5]. It is this intimate relationship between bond length (or, more general, the molecular potential), vibrational structure, and shape resonance phenomena that can now be studied systematically on core levels at very high spectral resolution.

Figure 3 shows two C 1s photoelectron spectra of CO covering a wider energy range in order to include the major part of the shakeup satellites. These spectra were measured at reduced energy resolution, but the vibrational structure in the C 1s main line is still visible. The satellites known from measurements in the "sudden" limit using monochromatized Al $K\alpha$ radiation have been labeled as in Ref. [22]. They all have the same symmetry as the main line, i.e., Σ^+ . More specifically, peaks 1 and 2 are due to excited states with the configuration $1s^{-1}1\pi^{-1}2\pi^1$ where the π and π^* electrons are triplet and singlet coupled, respectively; peaks 3–5 correspond to states of the type $1s^{-1}5\sigma^{-1}n\sigma^1$. Satellites labeled by letters a–d in Fig. 3 are only present in spectra measured near the C 1s threshold. They are therefore assigned to conjugate shakeup processes [9,23] leading to states of symmetry other than Σ^+ . Such states—as well as the Σ^+ states—have recently been calculated using a Green's function technique [23]; the energies and symmetries from this work are included in Fig. 3. Satellites a and b were also recently observed at threshold in the high reso-

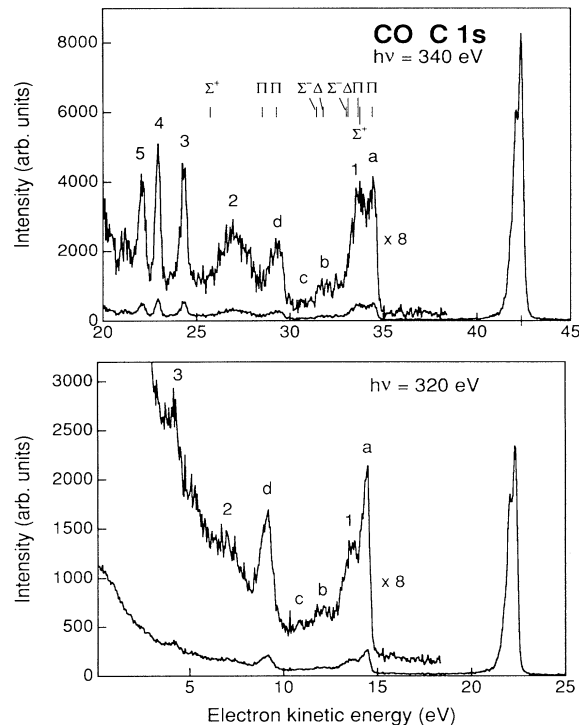


FIG. 3. C 1s photoelectron spectra of CO measured at $h\nu=340$ eV (top) and $h\nu=320$ eV (bottom), showing the region of shakeup satellites. The vertical bars represent the positions of direct and conjugate shakeup satellites predicted by Schirmer *et al.* and Angonoa, Walter, and Schirmer [22,23]. Note that the calculated energies have been shifted to make the lowest Σ^+ state coincide with satellite 1.

lution ZEKE work referred to above [13]; peaks c and d appear to have very little intensity at threshold [24]. The intense feature d is the only conjugate shakeup satellite in the C 1s spectrum of CO that is well resolved in near threshold photoelectron spectroscopy on conventional synchrotron radiation beam lines at low resolution [25].

Thus photon energy dependent measurements at high resolution also deliver important new information on the shakeup satellites. The most important result is that—within a range of ~ 30 eV from its threshold—the lowest conjugate shakeup satellite (a) with Π symmetry at a relative energy of ~ 7.9 eV is at least as intense as the triplet-coupled $\pi \rightarrow \pi^*$ satellite (1) at ~ 8.6 eV. Moreover, the unexpectedly large cross section enhancement of the first satellite structure on approaching threshold, which was previously attributed solely to the $\pi \rightarrow \pi^*$ Σ^+ state [10], is to a large extent due to the increasing intensity of the lowest Π satellite (but nevertheless satellite 1 appears to be more intense near threshold than satellite 2). This conclusion could not be drawn from the ZEKE spectrum alone since the additional satellite lines could have appreciable intensity only in a very small energy region (< 1 eV) above threshold. Such cases are

well documented for atoms [12]. In contrast, peak d in the C 1s spectrum shows the opposite behavior: It is already observed at relatively high photon energies, more than 70 eV above its threshold, and gains intensity continuously towards lower photon energies, becoming one of the strongest satellites between $h\nu=325$ eV and $h\nu=315$ eV. At threshold, however, its cross section is almost zero [24]. Thus CO also represents a prominent example for different photon energy dependence of shakeup satellites in the threshold region, suggesting the influence of several different factors. More detailed measurements at the magic angle as well as theoretical calculations are needed for a deeper understanding.

In summary, we report C 1s photoelectron spectra of CO measured with unprecedented resolution in the near threshold region. The measured vibrational energy of 301 ± 3 meV is close to the equivalent core value but smaller than that predicted theoretically. The σ^* shape resonance enhances higher vibrational states and leads to strong non-FC behavior. This case represents the first textbook example of this phenomenon in core level photoionization. Finally, the unambiguous identification of conjugate shakeup satellites and the determination of their evolution with photon energy lead to a complete reinterpretation of the direct satellite behavior of CO in particular and demonstrate the importance of different mechanisms for the near threshold behavior of shakeup satellites in general.

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*Present address: Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

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